

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Huy X. Nguyen et al.

Group Art Unit: (uncertain)

Serial No: 07/683,016

Examiner: (uncertain)

Filed: April 10, 1991

File No. 82-2775 CIP2

For: BALLISTIC RESISTANT COMPOSITE ARTICLE HAVING IMPROVED MATRIX
SYSTEM

May 30, 2008

VIA FAX 571-273-0185

Licensing and Review
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

PETITION TO RESCIND SECRECY ORDER UNDER 37 CFR §5.4

Applicants respectfully petition to rescind the Secrecy Order in this application. The Secrecy Order was originally issued on May 24, 1994. The Secrecy Order has been renewed over the years, the last time apparently on June 27, 2006. It is understood that the last renewal of the Secrecy Order was requested by the Department of the Army.

It is respectfully pointed out that the subject application is a continuation-in-part of application Serial Number 07/432,259 filed November 6, 1989. The parent application issued as U.S. Patent 5,330,820 on July 19, 2004 (copy attached for convenience).

The subject matter of the parent patent is directed to a composite material which includes two or more layers, wherein adjacent fibrous layers comprise a network of high

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Petition Under 37 CFR 5.4 to Rescind Secrecy Order
Serial No. 07/683,016

The subject matter of the present application adds to the disclosure of the parent application the feature that an initiating/compatibilization agent is added to the matrix resins. Thus, the allowed claims of the subject application recite a composite which includes two or more layers, with at least two layers being adjacent layers comprising a network of high strength filaments in a rigid matrix. The matrix is a blend of one or more thermoplastic resins, one or more thermosetting resins, and the initiating/compatibilization agent.

The additional subject matter disclosed in and claimed in the present continuation-in-part application is the initiating/compatibilization agent. The other elements have been disclosed and claimed in the parent patent. As can be seen, the predominate technology has already been publicly disclosed in the issued parent patent. It is respectfully submitted that the addition of the initiating/compatibilization agent to the matrix material does not raise a national security issue. Thus, it is respectfully submitted that the continuation of the Secrecy Order in this application is not warranted. It is noted that the Secrecy Order has been in place for almost 14 years and there is no reason to continue to maintain the Secrecy Order.

There is no contract between the Government and any of the principals under which the subject matter of this application or any significant part thereof was developed, or to which the subject matter is otherwise related.

In summary, it is respectfully requested that the Secrecy Order be reviewed and that it be rescinded for the above reasons. Should there be any questions at all, it is respectfully requested that the undersigned be contacted.

A duplicate of this Petition is attached as per 37 CFR §5.4 (a).

Petition Under 37 CFR 5.4 to Rescind Secrecy Order
Serial No. 07/683,016

Also attached is a change of address letter. It is respectfully requested that the decision on this Petition be sent to:

Honeywell International Inc.
Patent Services
101 Columbia Road
Morristown, NJ 07962

Respectfully submitted,

Huy X. Nguyen et al.

By: Roger H. Criss
Roger H. Criss
(Their Attorney)
Reg. No. 25,570
(239) 254-0971

Attachments

- (1) Duplicate Copy of Petition
- (2) Copy of USP 5,330,820
- (3) Change of Address Letter

Roger H. Criss, Esq.
1462 Via Portofino
Naples, FL 34108

I hereby certify that this correspondence is being sent by fax to: 571-273-0185 on May 30, 2008.

Roger H. Criss Date: May 30, 2008
Roger H. Criss

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Roger H. Criss Date: May 30, 2008
Roger H. Criss



US005330820A

United States Patent [19]

Li et al.

[11] Patent Number: **5,330,820**[45] Date of Patent: **Jul. 19, 1994**

[54] **BALLISTIC RESISTANT COMPOSITION
ARTICLE HAVING IMPROVED MATRIX
SYSTEM**

[75] Inventors: Hsin L. Li, Parsippany, N.J.; Leroy C. Lin, Richmond, Va.; Dusan C. Prevorsek, Morristown; Hong B. Chia, Parsippany, both of N.J.

[73] Assignee: AlliedSignal Inc., Morris Township, Morris County, N.J.

[21] Appl. No.: 432,259

[22] Filed: Nov. 6, 1989

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 379,396, Jul. 13, 1989, abandoned.

[51] Int. Cl.⁵ B32B 5/12

[52] U.S. Cl. 428/113; 428/224;
428/285; 428/290; 428/902; 428/911; 428/286;
428/295

[58] Field of Search 428/105, 113, 114, 224,
428/284, 285, 287, 280, 339, 902, 911, 286, 295

[56] **References Cited**

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"The Application of High-Modulus Fibers to Ballistic Protection", R. C. Laible, J. Macromol. Sci-Chem., A7(1), (1973) 295-322.

Primary Examiner—Donald P. Walsh

Assistant Examiner—Ngoclan T. Mai

[57]

ABSTRACT

An impact resistant rigid composite article comprising a fibrous layer comprising a network of filaments dispersed in a rigid matrix comprising one or more thermosetting resins and one or more thermoplastic resins.

29 Claims, No Drawings

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BALLISTIC RESISTANT COMPOSITION ARTICLE HAVING IMPROVED MATRIX SYSTEM

RELATED APPLICATIONS

This is a continuation-in-part of U.S. patent application Ser. No. 379,396, filed Jul. 13, 1989 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to ballistic resistant composite articles. More particularly, this invention relates to such articles having improved ballistic protection.

2. Prior Art

Ballistic articles such as bulletproof vests, helmets, structural members of helicopters and other military equipment, vehicle panels, briefcases, raincoats and umbrellas containing high strength fibers are known. Fibers conventionally used include aramid fibers such as poly(phenylenediamine terephthalamide), graphite fibers, nylon fibers, ceramic fibers, glass fibers and the like. For many applications, such as vests or parts of vests, the fibers are used in a woven or knitted fabric. For many of the applications, the fibers are encapsulated or embedded in a matrix material.

In "The Application of High Modulus Fibers to Ballistic Protection", R. C. Laible et al., *J. Macromol. Sci.-Chem.*, A7(1), pp. 295-322, 1973, it is indicated on p. 298 that a fourth requirement is that the textile material have a high degree of heat resistance. In an NTIS publication, AD-A018 958 "New Materials in Construction for Improved Helmets", A. L. Alesi et al., a multilayer highly oriented polypropylene film material (without matrix), referred to as "XP", was evaluated against an aramid fiber (with a phenolic/polyvinyl butyral resin matrix). The aramid system was judged to have the most promising combination of superior performance and a minimum of problems for combat helmet development. U.S. Pat. Nos. 4,403,012 and 4,457,985 disclose ballistic resistant composite articles comprised of networks of high molecular weight polyethylene or polypropylene fibers, and matrices composed of olefin polymers and copolymers, unsaturated polyester resins, epoxy resins, and other resins curable below the melting point of the fiber.

A. L. Lastnik, et al., "The Effect of Resin Concentration and Laminating Pressures on KEVLAR Fabric Bonded with Modified Phenolic Resin", Tech. Report NATICK/TR-84/030, Jun. 8, 1984; disclose that an interstitial resin, which encapsulates and bonds the fibers of a fabric, reduces the ballistic resistance of the resultant composite article.

U.S. Pat. Nos. 4,623,574 and 4,748,064 disclose a simple composite structure comprising high strength fibers embedded in an elastomeric matrix. The simple composite structure exhibits outstanding ballistic protection as compared to simple composites utilizing rigid matrices, the results of which are disclosed in the patents. Particularly effective are simple composites employing ultra-high molecular weight polyethylene and polypropylene such as disclosed in U.S. Pat. No. 4,413,110.

U.S. Pat. Nos. 4,737,402 and 4,613,535 disclose complex rigid composite articles having improved impact resistance which comprise a network of high strength fibers such as the ultra-high molecular weight polyethylene and polypropylene disclosed in U.S. Pat. No.

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4,413,110 embedded in an elastomeric matrix material and at least one additional rigid layer on a major surface of the fibers in the matrix. It is disclosed that the composites have improved resistance to environmental hazards, improved impact resistance and are unexpectedly effective as ballistic resistant articles such as armor.

SUMMARY OF THE INVENTION

One aspect of the present invention relates to a ballistic-resistant rigid composite comprised of one or more layers, at least one of said layers is a fibrous layer comprising a network of high strength filaments having a tenacity of at least about 7 grams/denier, a tensile modulus of at least about 160 grams/denier and an energy-to-break of at least about 8 joules/gram in a rigid matrix material, wherein said matrix material comprising one or more thermoplastic polymers and one or more thermosetting resin. The composites of this invention exhibit good handling characteristics and long shelf life and resist delamination due to impact. During the molding of the composites of this invention, no or substantially no mold cooling is required, and mold cycle times are short, preferably less than about 30 minutes.

DETAILED DESCRIPTION OF THE INVENTION

Composites of this invention comprise a network of filaments in a rigid matrix which comprises one or more thermoplastic polymers and one or more thermosetting resins.

The cross-section of filaments for use in this invention may vary widely. Useful filaments may have a circular cross-section, oblong cross-section or irregular or regular multi-lobal cross-section having one or more regular or irregular lobes projecting from the linear or longitudinal axis of the filament. In the particularly preferred embodiments of the invention, the filaments are of substantially circular or oblong cross-section and in the most preferred embodiments are of circular or substantially circular cross-section.

In the composite articles of this invention, the filaments may be arranged in networks having various configurations. For example, a plurality of filaments can be grouped together to form twisted or untwisted yarn bundles in various alignments. The filaments or yarn may be formed as a felt, knitted or woven (plain, basket, satin and crow feet weaves, etc.) into a network, fabricated into non-woven fabric, arranged in parallel array, layered, or formed into a woven fabric by any of a variety of conventional techniques. Among these techniques, for ballistic resistance applications we prefer to use those variations commonly employed in the preparation of aramid fabrics for ballistic-resistant articles. For example, the techniques described in U.S. Pat. No. 4,181,768 and in M. R. Silyquist et al., *J. Macromol. Sci.-Chem.*, A7(1), pp. 203 et. seq. (1973) are particularly suitable. In preferred embodiments of the invention, the filaments in each layer are aligned in a substantially parallel and unidirectional fashion, and the matrix material substantially coats the individual filaments.

The type of filaments used in the fabrication of the article of this invention may vary widely and can be metallic filaments, semi-metallic filaments, inorganic filaments and/or organic filaments. Preferred filaments for use in the practice of this invention are those having a tenacity equal to or greater than about 10 g/d, a tensile modulus equal to or greater than about 150 g/d and an

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energy-in-break equal to or greater than about 8 joules/gram. Particularly preferred filaments are those having a tenacity equal to or greater than about 20 g/d, a tensile modulus equal to or greater than about 500 g/d and energy-in-break equal to or greater than about 30 joules/grams. Amongst these particularly preferred embodiments, most preferred are those embodiments in which the tenacity of the filaments are equal to or greater than about 25 g/d, the tensile modulus is equal to or greater than about 1000 g/d, and the energy-to-break is equal to or greater than about 35 joules/grams. In the practice of this invention, filaments of choice have a tenacity equal to or greater than about 30 g/d, the tensile modulus is equal to or greater than about 1300 g/d and the energy-to-break is equal to or greater than about 40 joules/grams.

Filaments for use in the practice of this invention may be metallic, semi-metallic, inorganic and/or organic. Illustrative of useful inorganic filaments are those formed from S-glass, silicon carbide, asbestos, basalt, E-glass, alumina, alumina-silicate, quartz, zirconia-silica, ceramic filaments, boron filaments, carbon filaments, and the like. Exemplary of useful metallic or semi-metallic filaments are those composed of boron, aluminum, steel and titanium. Illustrative of useful organic filaments are those composed of aramids (aromatic polyamides), poly(m-xylylene adipamide), poly(p-xylylene sebacamide), poly(2,2,2-trimethyl-hexamethylene terephthalamide), poly(piperazine sebacamide), poly(metaphenylene isophthalamide) (Nomex) and poly(p-phenylene terephthalamide) (Kevlar) and aliphatic and cycloaliphatic polyamides, such as the copolyamide of 30% hexamethylene diammonium isophthalate and 70% hexamethylene diammonium adipate, the copolyamide of up to 30% bis-(amidocyclohexyl) methylene, terephthalic acid and caprolactam, polyhexamethylene adipamide (nylon 66), poly(ε-butyrolactam) (nylon 4), poly(9-aminonanoic acid) (nylon 9), poly(ε-aminocaproic acid) (nylon 6), poly(ε-caprolactam) (nylon 6), polycaprolactam (nylon 6), poly(p-phenylene terephthalamide), polyhexamethylene sebacamide (nylon 6,10), polyaminoundecanamide (nylon 11), polydodecanolactam (nylon 12), polyhexamethylene isophthalamide, polyhexamethylene terephthal amide, polycaprolactam, poly(nonamethylene azelamide) (Nylon 9,9), poly(decamethylene azelamide) (nylon 10,9), poly(decamethylene sebacamide) (nylon 10,10), poly[bis(4-aminocyclohexyl)methane 1,10-decanedicarboxamide] (Qiana)(trans), or combination thereof; and aliphatic, cycloaliphatic and aromatic polyesters such as poly(1,4-cyclohexyldiene dimethyl eneterephthalate) cis and trans, poly(ethylene-2,6-naphthalate), poly(1,4-cyclohexane dimethylene terephthalate) (trans), poly(decamethylene terephthalate), poly(ethylene terephthalate), poly(ethylene isophthalate), poly(ethylene oxybenzoate), poly(para-hydroxy benzoate), poly(β,β dimethylpropiolactone), poly(decamethylene adipate), poly(ethylene succinate) and the like.

Also illustrative of useful organic filaments are those composed of extended chain polymers formed by polymerization of α, β-unsaturated monomers of the formula:



wherein:

R₁ and R₂ are the same or different and are hydrogen, hydroxy, halogen, alkylcarbonyl, carboxy, alkoxy, carbonyl, heterocycle or alkyl or aryl either unsubstituted

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or substituted with one or more substituents selected from the group consisting of alkoxy, cyano, hydroxy, alkyl and aryl. Illustrative of such polymers of α,β-unsaturated monomers are polymers including polystyrene, polyethylene, polypropylene, poly(1-octadecene), polyisobutylene, poly(1-pentene), poly(2-methylstyrene), poly(4-methylstyrene), poly(1-hexene), poly(1-pentene), poly(4-methoxystyrene), poly(5-methyl-1-hexene), poly(4-methylpentene), poly(1-butene), poly(3-methyl-1-butene), poly(3-phenyl-1-propene), poly(vinyl chloride), polybutylene, polyacrylonitrile, poly(methyl pentene-1), poly(vinyl alcohol), poly(vinyl acetate), poly(vinyl butyral), poly(vinyl chloride), poly(vinylidene chloride), vinyl chloride-vinyl acetate chloride copolymer, poly(vinylidene fluoride), poly(methyl acrylate), poly(methyl methacrylate), poly(methacrylonitrile), poly(acrylamide), poly(vinyl fluoride), poly(vinyl formal), poly(3-methyl-1-butene), poly(1-pentene), poly(4-methyl-1-pentene), poly(1-hexene), poly(5-methyl-1-hexene), poly(1-octadecene), poly(vinyl cyclopentane), poly(vinylcyclohexane), poly(α-vinylnaphthalene), poly(vinyl methyl ether), poly(vinylethylether), poly(vinyl propylether), poly(vinyl carbazole), poly(vinyl pyrrolidone), poly(2-chlorostyrene), poly(4-chlorostyrene), poly(vinyl formate), poly(vinyl butyl ether), poly(vinyl octyl ether), poly(vinyl methyl ketone), poly(methylisopropenyl ketone), poly(4-phenylstyrene) and the like.

In the most preferred embodiments of the invention, composite articles include a filament network, which may include a high molecular weight polyethylene filament, a high molecular weight polypropylene filament, an aramid filament, a high molecular weight polyvinyl alcohol filament, a high molecular weight polyacrylonitrile filament or mixtures thereof. U.S. Pat. No. 4,457,985 generally discusses such high molecular weight polyethylene and polypropylene filaments, and the disclosure of this patent is hereby incorporated by reference to the extent that it is not inconsistent herewith. In the case of polyethylene, suitable filaments are those of molecular weight of at least 150,000, preferably at least one million and more preferably between two million and five million. Such extended chain polyethylene (ECPE) filaments may be grown in solution as described in U.S. Pat. No. 4,137,394 to Meihuizen et al., or U.S. Pat. No. 4,356,138 of Kavesch et al., issued Oct. 26, 1982, or a filament spun from a solution to form a gel structure, as described in German Off. 3,004,699 and GB 2051667, and especially described in U.S. patent application Ser. No. 572,607 of Kavesch et al., filed Jan. 20, 1984 (see EPA 64,167, published Nov. 10, 1982). As used herein, the term polyethylene shall mean a predominantly linear polyethylene material that may contain minor amounts of chain branching or comonomers not exceeding 5 modifying units per 100 main chain carbon atoms, and that may also contain admixed therewith not more than about 50 wt% of one or more polymeric additives such as alkene-1-polymers, in particular low density polyethylene, polypropylene or polybutylene, copolymers containing mono-olefins as primary monomers, oxidized polyolefins, graft polyolefin copolymers and polyoxymethylenes, or low molecular weight additives such as anti-oxidants, lubricants, ultraviolet screening agents, colorants and the like which are commonly incorporated by reference. Depending upon the formation technique, the draw ratio and tempera-

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tures, and other conditions, a variety of properties can be imparted to these filaments. The tenacity of the filaments should be at least 15 grams/denier, preferably at least 20 grams/denier, more preferably at least 25 grams/denier and most preferably at least 30 grams/denier. Similarly, the tensile modulus of the filaments, as measured by an Instron tensile testing machine, is at least 300 grams/denier, preferably at least 500 grams/denier and more preferably at least 1,000 grams/denier and most preferably at least 1,200 grams/denier. These highest values for tensile modulus and tenacity are generally obtainable only by employing solution grown or gel filament processes.

Similarly, highly oriented polypropylene filaments of molecular weight at least 200,000, preferably at least one million and more preferably at least two million may be used. Such high molecular weight polypropylene may be formed into reasonably well oriented filaments by the techniques prescribed in the various references referred to above, and especially by the technique of U.S. patent application Ser. No. 572,607, filed Jan. 20, 1984, of Kavesch et al. and commonly assigned. Since polypropylene is a much less crystalline material than polyethylene and contains pendant methyl groups, tenacity values achievable with polypropylene are generally substantially lower than the corresponding values for polyethylene. Accordingly, a suitable tenacity is at least 8 grams/denier, with a preferred tenacity being at least 11 grams/denier. The tensile modulus for polypropylene is at least 160 grams/denier, preferably at least 200 grams/denier. The particularly preferred ranges for the above-described parameters can advantageously provide improved performance in the final article.

High molecular weight polyvinyl alcohol filaments having high tensile modulus are described in U.S. Pat. No. 4,440,711 to Y. Kwon et al., which is hereby incorporated reference to the extent it is not inconsistent herewith. In the case of polyvinyl alcohol (PV-OH), PV-OH filament of molecular weight of at least about 200,000. Particularly useful PV-OH filament should have a modulus of at least about 300 g/d, a tenacity of at least 7 g/d (preferably at least about 10 g/d, more preferably at about 14 g/d, and most preferably at least about 17 g/d), and an energy-to-break of at least about 8 joules/gram. PV-OH filaments having a weight average molecular weight of at least about 200,000, a tenacity of at least about 10 g/d, a modulus of at least about 300 g/d, and an energy-to-break of about 8 joules/gram are more useful in producing a ballistic resistant article. PV-OH filament having such properties can be produced, for example, by the process disclosed in U.S. Pat. No. 4,599,267.

In the case of polyacrylonitrile (PAN), PAN filament of molecular weight of at least about 400,000. Particularly useful PAN filament should have a tenacity of at least about 10 g/d and an energy-to-break of at least about 8 joules/gram. PAN filament having a molecular weight of at least about 400,000, a tenacity of at least about 15 to about 20 g/d and an energy-to-break of at least 8 joules/gram is most useful in producing ballistic resistant articles; and such filaments are disclosed, for example, in U.S. Pat. No. 4,535,027.

In the case of aramid filaments, suitable aramide filaments formed principally from aromatic polyamide are described in U.S. Pat. No. 3,671,542, which is hereby incorporated by reference. Preferred aramid filament will have a tenacity of at least about 20 g/d, a tensile modulus of at least about 400 g/d and an energy-to-

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break at least about 8 joules/gram, and particularly preferred aramid filaments will have a tenacity of at least about 20 g/d, a modulus of at least about 480 g/d and an energy-to-break of at least about 20 joules/gram. Most preferred aramid filaments will have a tenacity of at least about 20 g/denier, a modulus of at least about 900 g/denier and an energy-to-break of at least about 30 joules/gram. For example, poly(phenylenediamine terephthalamide) filaments produced commercially by Dupont Corporation under the trade name of Kevlar® 29, 49, 129 and 149 having moderately high moduli and tenacity values are particularly useful in forming ballistic resistant composites. Also useful in the practice of this invention is poly(metaphenylene isophthalamide) filaments produced commercially by Dupont under the tradename Nomex.

The filaments are dispersed in a continuous phase of a rigid matrix material which preferably substantially coats each filament contained in the bundle of filament. The manner in which the filaments are dispersed may vary widely. The filaments may be aligned in a substantially parallel, unidirectional fashion, or filaments may be aligned in a multidirectional fashion with filaments at varying angles with each other. In the preferred embodiments of this invention, filaments in each layer are aligned in a substantially parallel, unidirectional fashion such as in a prepreg, pultruded sheet and the like.

The matrix material employed in the practice of this invention comprises one or more thermosetting resins and one or more thermoplastic resins, preferably as a blend of such resins. As used herein "thermoplastic resins" are resins which can be heated and softened, cooled and hardened limitless times without undergoing a basic alteration, and "thermosetting resins" are resins which do not tolerate thermal cycling and which cannot be resoftened and reworked after molding, extruding or casting and which attain new, irreversible properties when once set at a temperature which is critical to each resin.

The proportions of thermosetting material to thermoplastic material in the matrix may vary widely depending on a number of factors including whether the matrix material has any ballistic-resistant properties of its own, the rigidity of the thermoplastic and thermosetting resins, and upon the shape, heat resistance, shelf life, wear resistance, flammability resistance and other desired properties desired for the composite article. In general, the higher the proportion of the thermoplastic resin and the lower the proportion of the thermosetting resin in the matrix, the greater the toughness and impact resistance and the longer the shelf life of the composite. However, longer mold cycle times and mold cooling cycles may be required with greater amounts of the thermoplastic resin. Conversely, the lower the proportion of the thermoplastic resin and the higher the proportion of the thermosetting resin in the matrix, the greater the rigidity and the shorter the mold cycle times and mold cooling cycles of the composites. However, toughness and impact resistance of the composite may be decreased relative to those of composites having greater amounts of the thermoplastic resin, and the shelf life of the composites may be decreased relative to those of composites having greater amounts of the thermoplastic resin. Thus, the relative proportions of thermosetting resins and thermoplastic resins are selected to achieve the desired physical properties and process parameters.

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The choice of any thermosetting resin and thermoplastic resin for use in the formation of the matrix may vary widely depending on the desired characteristics of the composite. One important characteristic of the matrix material is its modulus which is preferably equal to or greater than about 500 psi (3,450 kPa). The upper limit for the modulus is not critical and usually the higher the modulus the more desirable are composite properties. In the preferred embodiments of the invention, the thermoplastic and thermosetting resins are selected such that the matrix material has a modulus equal to or greater than about 500 psi (3,450 kPa), and in the particularly preferred embodiments, these resins are selected such that the matrix material has a modulus equal to or greater than about 2,000 psi (13,800 kPa). In the most preferred embodiments of the invention, the thermoplastic and thermosetting resins are selected such that the matrix material has a modulus equal to or greater than about 5,000 psi (34,500 kPa).

In general, the amount of thermoplastic resin is from about 10 to about 90 vol% based on total volume of the matrix and the amount of thermosetting resin is from about 90 to about 10 vol% on the aforementioned basis. In the preferred embodiments of the invention the amount of thermoplastic resin is from about 20 to about 80 based on the total volume of the matrix and the amount of thermosetting resin is from about 80 to about 20 vol% on the aforementioned basis. In the particularly preferred embodiments, the amount of thermoplastic resin in the matrix is from about 25 to about 75 vol% based on the volume of matrix and the amount of thermosetting material is from about 75 to about 25 vol% on the aforementioned basis. In the most preferred embodiments of the invention, the amount of thermoplastic resin in the matrix is from about 30 to about 70 vol% based on the total volume of the matrix, and the amount of thermosetting resin in the matrix is from about 70 to about 30 vol% on the aforementioned basis.

Thermosetting resins useful in the practice of this invention may vary widely. Illustrative of useful thermosetting resins are alkyds such as those derived from esterification of polybasic acids, as for example, phthalic anhydride, fumaric acid, maleic anhydride, isophthalic acid, terephthalic acid, trimesic acid, hemimellitic acid, succinic anhydride, fatty acids derived from mineral or vegetable oils and the like, and polyhydric alcohols as for example glycerol, ethylene glycol, propylene glycol, pinacol, 1,4-butanediol, 1,3-propanediol, sorbitol, pentaerythritol, 1,2-cyclohexanediol and the like. Other useful thermosetting resins are acrylics such as crosslinkable polyacrylics, polyacrylates, epoxydiacrylates, urethane diacrylates and the like. Still other useful thermosetting resins are amino resins derived from reaction between formaldehyde and various amino compounds such as melamine, urea, aniline, ethylene urea, sulfonamide, dicyanodiamide and the like. Other useful thermosetting resins include urethanes derived from reaction of polyisocyanates or diisocyanates such as 2,6-tolylene diisocyanate, 2,4-tolylene diisocyanate, 4,4'-diphenyl-methane diisocyanate, 4,4'-dicyclohexyl-methane diisocyanate and the like, and polyols such as glycerin, ethylene glycol, diethylene glycol, trimethylolpropane, 1,2,6-hexanetriol, sorbitol, pentaerythritol and the like.

Exemplary of still other thermosetting resins useful in the practice of this invention are unsaturated polyesters derived from reaction of dibasic acids such as maleic

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anhydride, fumaric acid, adipic acid, azelaic acid and the like, and dihydric alcohols such as ethylene glycol and propylene glycol, 1,3-butyleneglycol, 2,3-butyleneglycol, diethylene glycol, dipropylene glycols and the like; and silicones such as dimethyldichlorosilane and the like.

Yet another class of useful thermosetting resins are epoxies based on saturated or unsaturated aliphatic, cycloaliphatic, aromatic and heterocyclic epoxides. Useful epoxides include glycidyl ethers derived from epichlorohydrin adducts and polyols, particularly polyhydric phenols. Another useful epoxide is the diglycidyl ether of bisphenol A. Additional examples of useful polyepoxides are resorcinol diglycidyl ether, 3,4-epoxy-6-methylcyclohexylmethyl-9,10-epoxystearate, 1,2-bis(2,3-epoxy-2-methylpropoxy)ethane, diglycidyl ether of 2,2-(p-hydroxyphenyl) propane, butadiene dioxide, dicyclopentadiene dioxide, pentaerythritol tetrakis(3,4-epoxycyclohexanecarboxylate), vinylcyclohexene dioxide, divinylbenzene dioxide, 1,5-pentadiol bis(3,4-epoxycyclohexane carboxylate), ethylene glycol bis(3,4-epoxycyclohexane carboxylate), 2,2-diethyl-1,3-propanediol bis(3,4-epoxycyclohexanecarboxylate), 1,6-hexanediol bis(3,4-epoxycyclohexanecarboxylate), 2-butene-1,4-diol bis(3,4-epoxy-6-methylcyclohexanecarboxylate), 1,1,1-trimethylolpropane tris(3,4-epoxycyclohexanecarboxylate), 1,2,3-propanetriol tris(3,4-epoxycyclohexanecarboxylate), dipropylene glycol bis(2-ethylexy-4,5-epoxycyclohexane-1,2-dicarboxylate), diethylene glycol bis(3,4-epoxy-6-methylcyclohexanecarboxylate), triethylene glycol bis(3,4-epoxycyclohexanecarboxylate), 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, 3,4-epoxy-1-methylcyclohexylmethyl 3,4-epoxy-1-methylcyclohexanecarboxylate, bis(3,4-epoxycyclohexylmethyl) pimelate, bis(3,4-epoxy-6-methylenecyclohexylmethyl) maleate, bis(3,4-epoxy-6-methylcyclohexylmethyl) succinate, bis(3,4-epoxycyclohexylmethyl) oxalate, bis(3,4-epoxy-6-methylcyclohexylmethyl) sebacate, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, bis(3,4-epoxycyclohexylmethyl) terephthalate, 2,2'-sulfonyldichloro bis(3,4-epoxycyclohexanecarboxylate), N,N'-ethylene bis(4,5-epoxycyclohexane-1,2-dicarboximide), di(3,4-epoxycyclohexylmethyl) 1,3-tolylenedicarboximate, 3,4-epoxy-6-methylcyclohexanecarboxaldehyde acetal, 3,9-bis(3,4-epoxycyclohexyl) spirobi(methadioxane), and the like.

Useful thermosetting resins also include phenolic resins produced by the reaction of phenols and aldehydes. Useful phenols include phenol, o-cresol, m-cresol, p-cresol, p-tertbutylphenol, p-tertbutylphenol, p-nonylphenol, 2,3-xilenol, 2,4-xilenol, 2,5-xilenol, 2,6-xilenol, 3,1-xilenol, 3,4-xilenol, resorcinol, bisphenol-A and the like. Useful aldehydes include formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, glyoxal, furfural and the like.

Other useful thermosetting resins are aromatic vinyl esters such as the condensation product of epoxide resins and unsaturated acids usually diluted in a compound having double bond unsaturation such as vinylaromatic monomer as for example styrene and vinyltoluene, and diallyl phthalate. Illustrative of useful vinyl esters are diglycidyl adipate, diglycidyl isophthalate, di(2,3-epoxybutyl) adipate, di(2,3-epoxybutyl) oxalate, di(2,3-epoxyhexyl) succinate, d(3,4-epoxybutyl) malate, d(2,3-epoxyoctyl) pimelate, di(2,3-epoxybutyl) phthalate, di(2,3-epoxyoctyl) tetrahydrophthalate, di(4,5-epoxy-dodecyl) malate, di(2,3-epoxybutyl) tere-

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phthalate, di(2,3-epoxypentyl) thioldipropionate, di(5,6-epoxy-tetradecyl) diphenyldicarboxylate, di(3,4-epoxyheptyl) sulphonyldibutylate, tri(2,3-epoxybutyl) 1,2,4 butanetricarboxylate, di(5,6-epoxypentadecyl) maleate, di(2,3-epoxybutyl) azelate, di(3,4-epoxybutyl) citrate, di(5,6-epoxyoctyl) cyclohexane-1,3-dicarboxylate, di(4,5-epoxyoctadecyl) malonate, bisphenol-A-fumaric acid polyester and the like.

Preferred thermosetting resins for use in the practice of this invention are vinyl esters, unsaturated polyesters, epoxies and phenolites. Particularly preferred thermosetting resins are vinyl esters, epoxies and phenolics, with vinyl esters being the thermosetting resin of choice.

Thermoplastic resins for use in the practice of this invention may also vary widely. Illustrative of useful thermoplastic resins are polylactones such as poly(pivalolactone), poly(ϵ -caprolactone) and the like; polyurethanes derived from reaction of diisocyanates such as 1,5-naphthalene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 2,4-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 4,4'-diphenylisopropylidene diisocyanate, 3,3'-dimethyl-4,4'-diphenyl diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, dianisidine diisocyanate, tolidine diisocyanate, hexamethylene diisocyanate, 4,4'-diisocyananodiphenylmethane and the like and linear long-chain diols such as poly(tetramethylene adipate), poly(ethylene adipate), poly(1,4-butylene adipate), poly(1,5-pentylene adipate), poly(1,3-butylene adipate), poly(ethylene succinate), poly(2,3-butylene succinate), polyether diols and the like; polycarbonates such as poly(methane bis(4-phenyl) carbonate), poly[1,1-ether bis(4-phenyl) carbonate], poly[diphenylmethane (4-phenyl) carbonate], poly[1,1-cyclohexane bis(4-phenyl) carbonate] and the like; poly sulfones; polyether ether ketones; polyamides such as poly(4-amino butyric acid), poly(hexamethylene adipamide), poly(6-aminohexanoic acid), poly(m-xylylene adipamide), poly(p-xylylene sebacamide), poly(2,2,2-trimethyl hexamethylene terephthalamide), poly(metaphenyleneisophthalamide) (Nomex), poly(p-phenylene terephthalamide) (Kevlar), and the like; polyesters such as poly(ethylene azelate), poly(ethylene-1,5-naphthalate), poly(1,4-cyclohexane dimethylene terephthalate), poly(ethylene oxybenzoate) (A-Tell), poly(parahydroxy benzoate) (Ekonol), poly(1,4-cyclohexylidene dimethylene terephthalate) (Kodel) (as), poly(1,4-cyclohexylidene dimethylene terephthalate) (Kodel) (trans), polyethylene terephthalate, polybutylene terephthalate and the like; poly(arylene oxides) such as poly(2,6-dimethyl-1,4-phenylene oxide), poly(2,6-diphenyl-1,4-phenylene oxide) and the like; poly(arylene sulfides) such as poly(phenylene sulfide) and the like; polyetherimides; thermoplastic elastomers such as polyurethane elastomers, fluoroelastomers, butadiene/acrylonitrile elastomers, silicone elastomers, polybutadiene, polyisobutylene, ethylene-propylene copolymers, ethylene-propylene-diene terpolymers, polychloroprene, polysulfide elastomers, block copolymers, made up of segments of glassy or crystalline blocks such as polystyrene, poly(vinyltoluene), poly(t-butyl styrene), polyester and the like and the elastomeric blocks such as polybutadiene, polyisoprene, ethylene-propylene copolymers, ethylene-butylene copolymers, polyether ester and the like as for example the copolymers in polystyrene-polybutadiene-polystyrene

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block copolymer manufactured by Shell Chemical Company under the trade name of Kraton; vinyl polymers and their copolymers such as polyvinyl acetate, polyvinyl alcohol, polyvinyl chloride, polyvinyl butyral, polyvinylidene chloride, ethylene-vinyl acetate copolymers, and the like; polyacrylics, polyacrylate and their copolymers such as polyethyl acrylate, poly(n-butyl acrylate), polymethyl methacrylate, polyethyl methacrylate, poly(n-butyl methacrylate), poly(n-propyl methacrylate), polyacrylamide, polyacrylonitrile, polyacrylic acid, ethylene-acrylic acid copolymers, methyl methacrylate-styrene copolymers, ethylene-ethyl acrylate copolymers, methacrylated budadiene-styrene copolymers and the like; polyolefins such as low density polyethylene, polypropylene, chlorinated low density polyethylene, poly(4-methyl-1-pentene) and the like; ionomers; and polyepichlorohydrins.

In the preferred embodiments of the invention, the thermoplastic material is selected from the group consisting of polyurethanes, polyvinyls, polystyrene-polyisoprene-polystyrene block copolymer thermoplastic elastomers, polyacrylics and polyolefins. In the particularly preferred embodiments of the invention the preferred thermoplastic material is a polyurethane.

The proportions of matrix to filament in the composite is not critical and may vary widely depending on a number of factors including, whether the matrix material has any ballistic-resistant properties of its own (which is generally not the case) and upon the rigidity, shape, heat resistance, wear resistance, flammability resistance mold cycle time, handling characteristics and other properties desired for the composite article. In general, the proportion of matrix to filament in the composite may vary from relatively small amounts where the amount of matrix is about 10% by volume of the filaments to, relatively large amounts where the amount of matrix is up to about 90% by volume of the filaments. In the preferred embodiments of this invention, matrix amounts of from about 15 to about 85% by volume are employed. All volume percents are based on the total volume of the composite. In the particularly preferred embodiments of the invention, ballistic-resistant articles of the present invention contain a relatively minor proportion of the matrix (e.g., about 10 to about 30% by volume of composite), since the ballistic-resistant properties are almost entirely attributable to the filament, and in the particularly preferred embodiments of the invention, the proportion of the matrix in the composite is from about 10 to about 30% by volume of filaments.

The articles of this invention can be fabricated using a number of procedures. In general, the layers are formed by molding the combination of the matrix material and filaments in the desired configurations and amounts by subjecting the combination to heat, and pressure during a mold cycle time. An advantage of those embodiments of this invention in which the thermosetting resin is a vinyl ester is that relative short mold cycle times and temperatures may be employed.

The filaments may be premolded by subjecting them to heat and pressure. For example, for extended chain polyethylene filaments, molding temperatures range from about 20° to about 150° C., preferably from about 80° to about 145° C., more preferably from about 100° to about 135° C. depending on the type of matrix material selected. The molding pressure may range from about 10 psi (69 kPa) to about 10,000 psi (69,000 kPa). A pressure between about 10 psi (69 kPa) and about 100

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psi (690 kPa), when combined with temperatures below about 100° C. for a period of time less than about 1.0 min., may be used simply to cause adjacent filaments to stick together. Pressures from about 100 psi to about 10,000 psi (69,000 kPa), when coupled with temperatures in the range of about 100 to about 155° C. for a time of between about 1 to about 5 min., may cause the filaments to deform and to compress together (generally in a film-like shape). Pressures from about 100 psi (690 kPa) to about 10,000 psi (69,000 kPa), when coupled with temperatures in the range of about 150° to about 155° C. for a time of between 1 to about 5 min., may cause the film to become translucent or transparent. For polypropylene filaments, the upper limitation of the temperature range would be about 10 to about 20° C. higher than for ECPE filament.

In the preferred embodiments of the invention, the filaments (premolded if desired) are precoated with the desired matrix material prior to being arranged in a network and molded as described above. The coating may be applied to the filaments in a variety of ways and any method known to those of skill in the art for coating filaments may be used. For example, one method is to apply the matrix material to the stretched high modulus filaments either as a liquid, a sticky solid or particles in suspension, or as a fluidized bed. Alternately, the matrix material may be applied as a solution or emulsion in a suitable solvent which does not adversely affect the properties of the filament at the temperature of application. In these illustrative embodiments, any liquid capable of dissolving or dispersing the matrix material may be used. However, in the preferred embodiments of the invention useful solvents include water, paraffin oils, ketones, alcohols, aromatic solvents or hydrocarbon solvents or mixtures thereof, with illustrative specific solvents including paraffin xylene, toluene and octane. The techniques used to dissolve or disperse the matrix in the solvents will be those conventionally used for the coating of thermoplastic resins on a variety of substrates.

Other techniques for applying the coating to the filaments may be used, including coating of the high modulus precursor (gel filament) before the high temperature stretching operation, either before or after removal of the solvent from the filament. The filament may then be stretched at elevated temperatures to produce the coated filaments. The gel filament may be passed through a solution of the appropriate matrix material, as for example an elastomeric material dissolved in paraffin oil, or an aromatic or aliphatic solvent, under conditions to attain the desired coating. Crystallization of the polymer in the gel filament may or may not have taken place before the filament passes into the cooling solution. Alternately, the filament may be extruded into a fluidized bed of the appropriate matrix material in powder form.

The proportion of coating on the coated filaments or fabrics may vary from relatively small amounts (e.g., 1% by weight of filaments) to relatively large amounts (e.g., 150% by weight of filaments), depending upon whether the coating material has any impact or ballistic-resistant properties of its own (which is generally not the case) and upon the rigidity, shape, heat resistance, wear resistance, flammability resistance and other properties desired for the complex composite article. In general, ballistic-resistant articles of the present invention containing coated filaments should have a relatively minor proportion of coating (e.g., about 10 to

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about 30 percent by volume of filaments), since the ballistic-resistant properties are almost entirely attributable to the filament. Nevertheless, coated filaments with higher coating contents may be employed. Generally, however, when the coating constitutes greater than about 60% (by volume of filament), the coated filament is consolidated with similar coated filaments to form a simple composite without the use of additional matrix material.

Furthermore, if the filament achieves its final properties only after a stretching operation or other manipulative process, e.g. solvent exchanging, drying or the like, it is contemplated that the coating may be applied to a precursor material of the final filament. In such cases, the desired and preferred tenacity, modulus and other properties of the filament should be judged by continuing the manipulative process on the filament precursor in a manner corresponding to that employed on the coated filament precursor. Thus, for example, if the coating is applied to the xerogel filament described in U.S. patent application Ser. No. 572,607 of Kavesh et al., and the coated xerogel filament is then stretched under defined temperature and stretch ratio conditions, then the filament tenacity and filament modulus values would be measured on uncoated xerogel filament which is similarly stretched.

It is a preferred aspect of the invention that each filament be substantially coated with the matrix material for the production of composites having improved impact protection, delamination resistance, rigidity and/or ballistic resistance, and relatively shorter mold cycle times, preferably of less than about 30 minutes. A filament is substantially coated by using any of the coating processes described above or can be substantially coated by employing any other process capable of producing a filament coated essentially to the same degree as a filament coated by the processes described heretofore (e.g., by employing known high pressure molding techniques).

The filaments and networks produced therefrom are formed into "simple composites" as the precursor to preparing the complex composite articles of the present invention. The term, "simple composite", as used herein is intended to mean composites made up of one or more layers, each of the layers containing filaments as described above with a single major matrix material, which material may include minor proportions of other materials such as fillers, lubricants or the like.

The proportion of matrix material to filament is variable for the simple composites, with matrix material amounts of from about 5% to about 150 vol%, by volume of the composite, representing the broad general range. Within this range, it is preferred to use composites having a relatively high filament content, such as composites having only about 10 to about 30 vol% matrix material by volume of the composite.

Stated another way, the filament network occupies different proportions of the total volume of the simple composite. Preferably, however, the filament network comprises at least about 30 volume percent of the simple composite. For ballistic protecting, the filament network comprises at least about 50 volume percent, more preferably about 70 volume percent, and most preferably at least about 75 volume percent, with the matrix occupying the remaining volume.

A particularly effective technique for preparing a preferred composite of this invention comprised of substantially parallel, unidirectional aligned filaments in-

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cludes the steps of pulling a filament or bundles of filaments through a bath containing a solution of a matrix material and circumferentially winding this filament into a single sheet-like layer around and along a bundle of filaments the length of a suitable form, such as a cylinder. The solvent, if used, is then evaporated leaving a sheet-like layer of filaments embedded in a matrix that can be removed from the cylindrical form. Alternatively, a plurality of filaments or bundles of filaments can be simultaneously pulled through the bath containing a solution or dispersion of a matrix material and laid down in closely positioned, substantially parallel relation to one another on a suitable surface. Evaporation of the solvent leaves a sheet-like layer comprised of uni-directional filaments which are coated with the matrix material and which are substantially parallel and aligned along a common filament direction. The sheet is suitable for subsequent processing such as laminating to another sheet to form composites containing more than one layer.

Similarly, a filament-type simple composite can be produced by pulling a group of filament bundles through a dispersion or solution of the matrix material to substantially coat each of the individual filaments, and then evaporating the solvent to form the coated yarn. The yarn can then, for example, be employed to form fabrics, which in turn, can be used to form more complex composite structures. Moreover, the coated yarn can also be processed into a simple composite by employing conventional filament winding techniques; for example, the simple composite can have coated yarn formed into overlapping filament layers.

The number of layers included in the composite of this invention may vary widely depending on the uses of the composite, for example, in those uses where the composite would be used as ballistic protection, the number of layers would depend on a number of factors including the degree of ballistic protection desired and other factors known to those of skill in the ballistic protection art. In general for this application, the greater the degree of protection desired the greater the number of layers included in the article for a given weight of the article. Conversely, the lesser the degree of ballistic protection required, the lesser the number of layers required for a given weight of the article. It is convenient to characterize the geometries of such composites by the geometries of the filaments and then to indicate that the matrix material may occupy part or all of the void space left by the network of filaments. One such suitable arrangement is a plurality of layers or laminates in which the coated filaments are arranged in a sheet-like array and aligned parallel to one another along a common filament direction. Successive layers of such coated, uni-directional filaments can be rotated with respect to the previous layer. An example of such laminate structures are composites with the second, third, fourth and fifth layers rotated +45°, -45°, 90° and 0°, with respect to the first layer, but not necessarily in that order. Other examples include composites with 0°/90° layout of yarn or filaments.

One technique for forming composites of this invention having more than one layer includes the steps of arranging coated filaments into a desired network structure, and then consolidating and heat setting the overall structure to cause the coating material to flow and occupy the remaining void spaces, thus producing either a continuous or a discontinuous matrix without a mold cooling cycle or with a relatively short mold cooling

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cycle. Another technique is to arrange layers or other structures of coated or uncoated filament adjacent to and between various forms, e.g. fabric films, of the matrix material and then to consolidate and heat set the overall structure. In the above cases, it is possible that the matrix can be caused to stick or flow without completely melting. In general, if the matrix material is caused to melt, relatively little pressure is required to form the composite; while if the matrix material is only heated a sticking point, generally more pressure is required. Also, the pressure and time to set the composite and achieve optimal properties will generally depend on the nature of the matrix material (chemical composition as well as molecular weight) and processing temperature.

The composites of this invention comprising one or more layers may be incorporated into complex composites. For example, such composites may be incorporated into more complex composites to provide a more rigid complex composite article suitable, for example, as structural ballistic-resistant components, such as helmets, structural members of aircraft, and vehicle panels. The term "rigid" as used in the present specification and claims, is intended to include semi-flexible and semi-rigid structures that are capable of being free standing, without collapsing. To form the complex composite, at least one substantially rigid layer is bonded or otherwise connected to a major surface of the mono or multi-layer composite. The resultant complex composite article is capable of standing by itself and is impact and delamination resistant. Where there is only one layer, the composite of this invention ordinarily forms a remote portion of the complex composite article; that is a portion that is not initially exposed to the environment, e.g., the impact of an oncoming projectile. Where there is more than one layer, the simple composite may form, for example, a core portion that is sandwiched between two or more rigid layers, as is particularly useful, for example, in helmet applications. Other forms of the complex composite are also suitable, for example a composite comprising multiple alternating layers of simple composite and rigid layer.

In the preferred embodiments of the invention, rigid layers are preferably comprised of an impact resistant material, such as steel plate, composite armor plate, ceramic reinforced metallic composite, ceramic plate, concrete, and high strength filament composites (for example, an aramid, polyethylene or glass filament and a high modulus, resin matrix such as an epoxy resin, a phenolic resin, a vinyl ester resin, an unsaturated polyester, nylon 6, nylon 6,6 and polyvinylidene halide). Most preferably, the rigid impact resistant layer is one which is ballistically effective, such as ceramic plates or ceramic reinforced metal composites. A desirable embodiment of our invention is the use of a rigid impact resistant layer which will at least partially deform the initial impact surface of the projectile or cause the projectile to shatter such as aluminum oxide, boron carbide, silicon carbide and beryllium oxide (see Laible, supra, Chapters 5-7 for additional useful rigid layers). For example, a particularly useful ballistic resistant complex composite comprises a simple composite comprising highly-oriented high molecular weight polyethylene filament in a matrix on which is formed at least one layer comprising a material which may be heat resistant, flame resistant, solvent resistant, radiation resistant, or combinations thereof such as stainless steel, copper, aluminum oxides, titanium, titanium boride and the like.

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A portion of the rigid impact resistant composite, the volume percent of the simple composite is variable depending upon the desired properties of the final product. The volume percent of the simple composite to the complex composite is ordinarily at least about 10%, preferably at least about 15%, and most preferably at least 20% (for maximizing ballistic resistance). The volume percent of the simple composite to the complex composite is ordinarily at least about 5%, preferably at least about 10%, and most preferably at least about 15% (for maximizing ballistic resistance). The examples illustrate the effectiveness of a simple composite in a complex structure at various percentages of the simple composite to the total. For example, various compromises between structural rigidity and ballistic performance are attainable depending upon the specific material choices and the relative properties of the simple composites and rigid layers.

The multilayer composites of this invention exhibits enhanced peel strength as compared to conventional multilayer composites which results in reduced delamination of the composite on impact. In the preferred embodiments of the invention, peel strength between at least two adjacent layers of the multilayer composite is at least about 1.5 lbs/in as determined by the peel resistance test of ASTM-D-1876-72, and in the more preferred embodiments of the invention, the peel strength between at least two adjacent layers of the composite is equal to or greater than about 3 lbs/in. In the most preferred embodiments of the invention, the peel strength between at least two adjacent layers of the composite is equal to or greater than about 6 lbs/in, with those multilayer composites having layer peel strength equal to or greater than about 8 lbs/in being the composites of choice.

The composites of this invention can be used for conventional purposes. For example, such composites can be used in the fabrication of structural parts, ballistic armor and the like using conventional methods.

The following examples are presented to provide a more complete understanding of the invention and are not to be construed as limitations thereon. In the examples, the following technical terms are used:

(a) "Areal Density" which is the weight of the armor material per unit area usually in Kg/m² or lb/ft².

(b) "V₅₀" which is the projectile velocity which is statistically at the borderline penetration and partial penetrations which has a 50% probability of penetrating the target. The specific techniques, conditions, materials, proportions and reported data set forth to illustrate the principles of the invention are exemplary and should not be construed as limiting the scope of the invention.

EXAMPLE I

This example illustrates the advantages of using a homogeneous blend of a thermoplastic polyurethane and a thermoset vinyl/ester as the matrix-resin system. The resin system is formulated as shown in the following Table I.

TABLE I

Components	weight (g)	solids, weight (g)
1 Durethane 8084 ^(a)	60	30
2 Diallyl phthalate monomer	12	12
3 Lupersol 256 ^(b)	0.36	0.36

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TABLE I-continued

Components	weight (g)	solids, weight (g)
4 Dispercoll E585 ^(c)	175	70

^(a)-Durethane 8084[®] is an aqueous dispersion of ester/styrene monomer (50/50 w/w) manufactured and sold by Dow Chemical Company.
^(b)-Lupersol 256[®] is 2,5-dimethyl-2,4-di-2-ethylhexanoylperoxyhexane manufactured and sold by Penwalt Corporation.
^(c)-Dispercoll E585[®] is an aqueous dispersion of a thermoplastic polyurethane manufactured and sold by Mobay Corporation.

The above resin components were homogeneously mixed within a container. Water was then added to achieve the proper viscosity level suitable for coating the filaments. The weight ratio between thermoplastic polyurethane (Dispercoll E585), and thermoset vinyl ester (calculated based on the solid content basis) was 70/30. Using this resin and Spectra - 1000 yarns of 650 deniers/118 filaments, uniaxial prepreg tapes were produced. The prepreg tapes (12 inch (30.4 cm) × 0.0025 inch (0.0064 cm) contained approximately 75% weight fibers and 25% weight resin. The prepreg tapes were cut into 12" (30.4 cm) × 12" (30.4 cm) layers which were subsequently stacked into 0°, 90° yarn orientation between adjacent layers. A panel consisting of 132 layers was molded under pressure of approximately 400 psi (2758 kpa) at a temperature of 115° C. for a mold cycle time of 20 minutes. The molded panel was then removed from the mold at 115° C. without any mold cooling. The panel surface appeared flat without any visual distortion.

The molded panel is rigid and had an areal density of 1.42 lbs./ft² (6.9 Kg/m²) and a V₅₀ of 2,206 K/m²/sec (673 m/sec) against fragment simulators.

The flexural properties of the panels under 72° F. (22° C.), 160° F. (71° C.) for 72 hours and -60° F. (-45° C.) for 72 hours were determined using the procedure of ASTM-D-790. The results are summarized in the following Table II.

TABLE II

Environmental Treatment	Stress at 5% Strain psi (kPa)	Flexural Modulus psi (KPa)
1 72° F. (22° C.)	4,510 (31,100)	947,000 (6.5 × 10 ⁶)
2 160° F. (71° C.) 72 hrs. oven, hot air	5,030 (34,700)	1,190,000 (8.2 × 10 ⁶)
3 -90° F. (-68° C.) 72 hrs. freezer	4,050 (27,900)	896,000 (6.2 × 10 ⁶)

EXAMPLE II

Example I was repeated except that the ratio of polyurethane to vinyl ester based on Solid content was 40/60. Uniaxial prepreg tapes made with the 40/60 composition were difficult to handle because of the stickiness during cut and stack sequence.

EXAMPLE III

Example I was repeated except that the ratio of polyurethane/vinyl ester was 90/10. Uniaxial prepreg tapes were easily cut and stacked into 12" (30.4 cm) × 12" (30.4 cm) layers. The molded panels were, however, very soft and severe deformation was observed when removed from the mold at a temperature of 115° C. which was above the solidification temperature of polyurethane. However, the molded panels were removed easily without any visual distortion if the mold was cooled down from 115° C. to room temperature of

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23° C. The panel had an areal density of 1.3 lbs/ft² (6.3 Kg/cm²). The ballistic V₅₀ performance was 2,316 ft/sec (706 m/sec).

EXAMPLE IV

Example I was repeated except that Spectra -1000 fabric was impregnated with a blend of polyurethane/vinyl ester in a 70/30 ratio. The fabrics/prepreg consisted of about 25% resin and 75% Spectra® - 1000 fabric. A panel (12" (30.4 cm)×12" (30.4 cm)) was molded from 20 layers of fabric prepreg at a temperature of 115° C. and a pressure of 400 psi (2,760 kPa) for 20 minutes without mold cooling cycle. The panel was then cut into 1" (2.54 cm)×12" (30.4 cm) strips. The peel resistance test, or T-peel test, was carried out according to the standard method outlined in ASTM-D-1876-72. At an Instron speed of 0.2" (0.5 cm) per minute, the peel strength was 5 lbs. per linear inch (0.89 kg/cm) which is far stronger than 1.5 lbs. per linear inch for strips molded from fabrics impregnated with vinyl ester resin under otherwise identical conditions. Higher peel strength represents higher interfacial adhesion which resists delamination upon impact.

What is claimed is:

1. An impact resistant composite comprised of two or more layers; at least two of said layers being two adjacent fibrous layers each comprising a network of filaments having a tensile modulus of at least about 150 g/denier, an energy-to-break of at about 8 j/d and a tenacity equal to or greater than about 7 g/denier in a rigid matrix wherein said matrix comprises one or more thermosetting resins and one or more thermoplastic resins wherein the weight % ratio of thermosetting resins to thermoplastic resins based on solids content is selected such that

peel strength between adjacent fibrous layers is at least about 3.0 lbs/in as determined by the peel resistance test of ASTM-D-1876-72.

2. A composite as recited in claim 1 wherein the filaments have a tenacity equal to or greater than about 10 g/d, a tensile modulus equal to or greater than about 300 g/d and an energy-to-break equal to or greater than about 10 j/g.

3. A composite as recited in claim 2 wherein said tenacity is equal to or greater than about 20 g/d, said modulus is equal to or greater than about 500 g/d and said energy-to-break is equal to or greater than about 15 j/g.

4. A composite as recited in claim 3 wherein said tenacity is equal to or greater than about 25 g/d, said modulus is equal to or greater than about 1000 g/d, and said energy-to-break is equal to or greater than about 20 j/g.

5. A composite as recited in claim 4 wherein said tenacity is equal to or greater than about 30 g/d, said modulus equal to or greater than about 1300 g/d and the energy-to-break is equal to or greater than about 30 j/g.

6. A composite as recited in claim 1 wherein filaments are polyethylene filaments having a tensile modulus of at least about 800 g/denier and an energy-to-break of at least 35 j/g.

7. A composite as recited in claim 1 wherein said peel strength is equal to or greater than about 6 lbs/in.

8. A composite as recited in claim 7 wherein said peel strength is equal to or greater than about 8 lbs/in.

9. A composite as recited in claim 1 wherein said network of filaments comprises a sheet-like filament array in which said filaments are arranged substantially parallel to one another along a common filament direction.

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10. A composite as recited in claim 9 wherein said composite comprises more than one layer, with adjacent layers aligned 90° which respect to the longitudinal axis of the parallel filaments contained in said layers.

11. A composite as recited in claim 1 wherein said network of filaments comprises a non-woven fabric.

12. A composite as recited in claim 1 wherein said network of filaments comprises a woven fabric.

13. A composite as recited in claim 1 wherein the volume fraction of said filaments is at least about 0.4.

14. A composite as recited in claim 1 wherein said matrix material comprises one or more thermosetting resins selected from the group consisting of vinyl esters, phenolic, epoxies, allylics, urethanes, unsaturated polyesters and alkyds, and one or more thermoplastic resins selected from the group consisting of polyamides, polystyrene-polyisoprene-polystyrene block copolymer, polyacrylics, polycarbonates, polyurethanes, polyarylene oxides, polyarylene sulfones, polyarylene sulfides, polyacetals, polyvinyl acetate, polyether ether ketones, polyaramids, polyesteramides, and polyimides.

15. A composite as recited in claim 14 wherein said thermosetting resins are selected from the group consisting of vinyl esters, phenolics and epoxies, and said thermoplastic resins are selected from the group consisting of polyurethanes and polyamides.

16. A composite as recited in claim 1 wherein said matrix comprises a thermoplastic polyurethane and a thermosetting vinyl ester.

17. A composite as recited in claim 1 wherein the matrix comprises a thermoplastic polystyrene-polyisoprene-polystyrene block copolymer and thermoset vinyl ester.

18. A composite according to claim 1 wherein the modulus of said matrix material is equal to or greater than about 3,450 kPa.

19. A composite according to claim 1 which further comprises at least one layer of a hard rigid material.

20. A composite according to claim 19 wherein said rigid material is selected from the group consisting of metals, ceramics, and glass reinforced polymers.

21. A composite as recited in claim 2 wherein said mold cycle times are equal to or less than about 20 minutes.

22. A composite as recited in claim 1 wherein said matrix comprises one thermosetting resin and one thermoplastic resin wherein said thermosetting resin is a vinyl ester and said thermoplastic resin is a polyurethane, and wherein said weight ratio is greater than about 60:40 to no more than 90:10.

23. A composite as recited in claim 1 wherein said ratio is from less than about 60:40 to about 30:70.

24. A composite as recited in claim 22 wherein said filaments are polyethylene filaments, aramid filaments or a combination thereof.

25. A composite as recited in claim 23 wherein said filaments are polyethylene filaments, aramid filaments or a combination thereof.

26. A composite as recited in claim 25 wherein said filaments are polyethylene filaments.

27. A composite as recited in claim 25 wherein said filaments are aramid filaments or a combination of aramid filaments and polyethylene filaments.

28. A composite as recited in claim 26 wherein said ratio is about 30:70.

29. A composite as recited in claim 1 wherein said weight ratio is selected such that during the molding of said composite no or substantially no mold cooling is required and mold cycle times are less than about 30 minutes.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,330,820
DATED : July 19, 1994
INVENTOR(S) : LI ET AL.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Col. 17, line 56, insert --said-- between the words "wherein" and "filaments".

Col. 18, line 31, insert --a-- between the words "and" and "thermoset".

Signed and Sealed this
Twenty-fifth Day of October, 1994

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks